

# PATENT ABSTRACTS OF JAPAN

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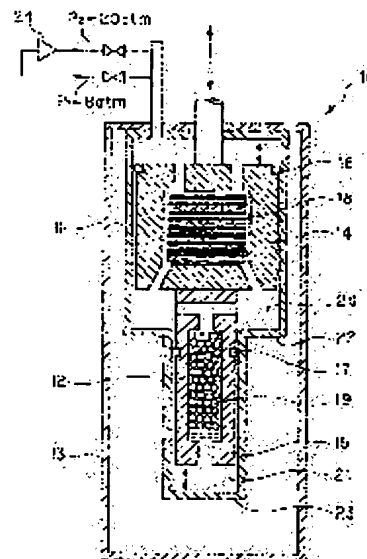
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## (54) COLD STORAGE MATERIAL AND COLD STORAGE TYPE REFRIGERATOR USING THE SAME

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a cold storage material capable of stably exhibiting remarkable freezing ability over a long period of time in an ultracold area and a cold storage type refrigerator, etc., using the material.

**SOLUTION:** The cold storage material 19 comprises a magnetic material represented by the general formula:  $R1-x(Ge1-yMy)x$  (wherein R is at least one kind of rare earth element selected from Y, La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb; M is at least one kind of element selected from Ag, Au, Al, Ga, In, Sn, Bi, Pd, Pt, Zn, Rh, Ir, Ru, Mn, Cr, Mo, W, V, Nb, Ta, Ti, Zr and Hf; x and y each satisfy the formulas  $0.1 \leq x \leq 0.8$  and  $0 \leq y \leq 0.5$  in the atom ratio).



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CLAIMS

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[Claim(s)]

[Claim 1]

General formula :  $R1-x(\text{germanium}1-y\text{My})x$  (however, R shows at least a kind of rare earth elements chosen from Y, La, Ce, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) M shows at least a kind of element chosen from Ag, Au, aluminum, Ga, In, Sn, Bi, Pd, Pt, Zn, Rh, Ir, Ru, Mn, Cr, Mo, W, V, Nb, Ta, Ti, Zr, and Hf. x and y are satisfied with an atomic ratio of  $0.1 \leq x \leq 0.8$  and  $0 \leq y \leq 0.5$ , respectively. The cold reserving material characterized by consisting of the magnetic substance expressed.

[Claim 2]

The cold reserving material characterized by the range of the atomic ratio x in said general formula being 0.5–0.7 in a cold reserving material according to claim 1.

[Claim 3]

The cold reserving material characterized by the range of the atomic ratio x in said general formula being 0.6–0.7 in a cold reserving material according to claim 1.

[Claim 4]

The cold reserving material characterized by the particle size of the magnetic particle which constitutes a cold reserving material being 0.01–3mm in a cold reserving material according to claim 1.

[Claim 5]

The cold reserving material characterized by the rate of the magnetic particle which the ratio (aspect ratio) to the minor axis of a major axis is five or less, and has the particle size of 0.01mm or more 3mm or less to all the magnetic particles that constitute a cold reserving material being more than 70 mass % in a cold reserving material according to claim 1.

[Claim 6]

In the cool storage type refrigerator which has two or more cooling stages which consist of the regenerator filled up with the cold reserving material, pours an actuation medium from the upper elevated-temperature side of the regenerator of each cooling stage, and obtains whenever [ low-temperature ] more in the downstream of regenerator by the heat exchange of the above-mentioned actuation medium and a cold reserving material The cool storage type refrigerator characterized by some [ at least ] cold reserving materials of the cold reserving material with which the low temperature side space of the regenerator of an aftercooling stage is filled up consisting of a cold reserving material according to claim 1 to 5.

[Claim 7]

The super-conductive magnet characterized by providing a cool storage type refrigerator according to claim 6.

[Claim 8]

MRI (nuclear-magnetic-resonance imaging) equipment characterized by providing a cool storage type refrigerator according to claim 6.

[Claim 9]

Cryopump characterized by providing a cool storage type refrigerator according to claim 6.

[Claim 10]

Field impression type crystal pulling equipment characterized by providing a cool storage type refrigerator according to claim 6.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the cool storage type refrigerator which used a cold reserving material and this, and relates to the cool storage type refrigerator which used the cold reserving material which can demonstrate remarkable refrigerating capacity in 20K or less super-low temperature range especially, and its cold reserving material.

[0002]

[Description of the Prior Art]

In recent years, development of a superconduction technique is remarkable, the applicable field follows on expanding, it is small and development of the refrigerator of high performance is becoming indispensable. It is required that this small refrigerator should be lightweight and small and thermal efficiency should be high, and utilization is advanced in various applicable fields.

[0003]

For example, in superconduction MRI equipment, cryopump, etc., the refrigerator by refrigerating cycles, such as a Gifford McMahon packing (GM) method and the Stirling method, is used. Moreover, in order to use a super-conductive magnet also for a maglev train and to generate magnetism, the highly efficient refrigerator is made indispensable. Furthermore, recently also in the single crystal raising equipment in a magnetic field which manufactures superconduction stationary-energy-storage equipment (SMES), the silicon wafer of high quality, etc., the highly efficient refrigerator is used.

[0004]

In such a refrigerator, actuation media, such as helium gas compressed in the inside of the regenerator with which the cold reserving material was filled up, flow to an one direction, the heat energy is supplied to a cold reserving material, the actuation medium which expanded here flows to an opposite direction, and heat energy is received from a cold reserving material. The recuperation effectiveness in such a process follows on becoming good, the thermal efficiency in an actuation medium cycle improves, and it becomes possible to realize lower temperature.

[0005]

As a cold reserving material used for a refrigerator which was mentioned above, Cu, Pb, etc. have mainly been used conventionally. Since the specific heat becomes remarkably small by 20K or less very low temperature, the recuperation effectiveness mentioned above does not fully function, but it becomes impossible however, to store sufficient heat energy for a cold reserving material for every cycle under very low temperature, and for such a cold reserving material to receive heat energy with an actuation medium sufficient from a cold reserving material on the occasion of actuation with a refrigerator. Consequently, in the refrigerator incorporating the regenerator filled up with said cold reserving material, there was a problem which very low temperature cannot be made to reach.

[0006]

So, recently, in order to improve the recuperation property in the very low temperature of said regenerator and to realize frozen temperature more near an absolute zero-point, the magnetic

cold reserving material which made the subject especially the intermetallic compound which has the maximal value of volume ratio heat, and consists of rare earth elements and a transition-metals element like Er<sub>3</sub>Ni with the big value, ErNi, and HoCu<sub>2</sub> in 20K or less super-low temperature range is used. Refrigeration by 4K is realized by using such a magnetic cold reserving material for the GM refrigerator.

[0007]

Moreover, the magnetic substance which consists of rare-earth-elements [ at least one sort of ] 35 - 95at% and additive [ which contains Si at least ] 5 - 65at% is indicated by JP,8-178443,A (patent reference 1 reference). Moreover, making an additive contain at least one sort of elements, such as B, aluminum, In, and germanium, is indicated by the above-mentioned patent reference 1.

[0008]

[Patent reference 1]

JP,8-178443,A (the 1-2nd page, claim 2)

[0009]

[Problem(s) to be Solved by the Invention]

However, it is difficult for the above-mentioned patent reference 1 not to indicate at all the example which made the additive contain germanium element, but to grasp the use. On the other hand, it follows on applying the above refrigerators to various systems being examined more concretely, the technical request which cools a cooling object with a more big scale in the condition of having been stabilized for a long period of time increases, and improvement in much more refrigerating capacity is called for.

[0010]

By the way, in the case of the regenerator of the aftercooling stage of a cool storage type refrigerator which generally has two or more cooling stages, i.e., a two-step expansion type refrigerator, in the interior of the regenerator of the 2nd step, while the temperature of the elevated-temperature side edge section into which an actuation medium flows is about 30K, a temperature gradient is formed so that the temperature of the down-stream low-temperature side edge section may become about 4K.

[0011]

Throughout the above broad temperature regions, since the cold reserving material with big volume ratio heat does not exist, it fills up with the cold reserving material which has a suitable specific heat property for each temperature region actually corresponding to the temperature distribution inside regenerator, respectively. That is, while volume ratio heat fills up a large cold reserving material with the broadest possible temperature field by the side of low temperature like HoCu<sub>2</sub>, like for example, Er<sub>3</sub>Ni, the laminating of the cold reserving material with large volume ratio heat is carried out, and it is filled up into the low temperature side of regenerator with the broad temperature field by the side of an elevated temperature at the elevated-temperature side.

[0012]

The key factor which has big effect on the refrigerator engine performance in about 4K super-low temperature range here is the class of cold reserving material with which the low temperature side of regenerator is filled up. By current, the cold reserving material which has the various presentations of ErNi<sub>2</sub>, ErNi<sub>0.9</sub>Co 0.1, ErNi<sub>0.8</sub>Co 0.2, ErRh, HoCu<sub>2</sub>, etc. as a cold reserving material with which the low temperature side of the above-mentioned regenerator is filled up is examined and tried. When the 2nd step cool storage machine of the usual two-step expansion type GM refrigerator is filled up with these cold reserving materials, it is HoCu<sub>2</sub> that the refrigerating capacity in 4K becomes the largest. However, since the volume ratio heat in the very-low-temperature field of 4K neighborhood of these cold reserving materials was still inadequate, neither has attained the remarkable improvement in refrigerating capacity.

[0013]

Moreover, when the cold reserving material which consists of ferromagnetics, such as ErNi<sub>2</sub>, ErNi<sub>0.9</sub>Co 0.1, and ErNi<sub>0.8</sub>Co0.2, was applied to the refrigerator for superconduction systems,

there was also a trouble that a possibility of it being easy to be influenced of the leakage magnetic field from a super-conductive magnet, for example, magnetism acting on the component part of a refrigerator, and producing partial wear and deformation became high.  
[0014]

While there is the advantage which the cold reserving material which consists of ErRh is the antiferromagnetic substance on the other hand, and cannot be easily influenced of the above-mentioned leakage magnetic field, the rhodium (Rh) as a constituent is very expensive, and putting in practical use industrially as a cold reserving material of the refrigerator used to hundreds of g order also had the trouble of being very difficult.

[0015]

It is made in order that this invention may solve the above-mentioned trouble, and it aims at offering the cool storage type refrigerator using the cold reserving material and it which it continues, and it is stabilized and can demonstrate remarkable refrigerating capacity in a super-low temperature range at a long period of time etc. [ the specific heat in the temperature region where the 4 - 6K neighborhood was restricted especially is large, and ] Furthermore, it aims at offering the MRI equipment which made it possible to demonstrate the engine performance which continued and was excellent in the long period of time, the super-conductive magnet for maglev trains, cryopump, and field impression type crystal pulling equipment by using the above cool storage type refrigerators.

[0016]

[Means for Solving the Problem]

In order to attain the above-mentioned purpose, this invention persons prepared the cold reserving material which has various presentations and a specific heat property, filled up the regenerator of a refrigerator, and did comparison examination of the effect the above-mentioned presentation and a specific heat property affect the refrigerating capacity of a refrigerator, the life of a cold reserving material, and endurance by experiment.

[0017]

Consequently, in the temperature region where the 4 - 6K neighborhood was restricted especially, the knowledge that the refrigerating capacity of a refrigerator [ in / by / to regenerator / being filled up / according to the specific heat property by the side of the elevated temperature / for a cold reserving material with large volume ratio heat / 4K temperature region ] improved notably was acquired. For example, while the specific heat in 4K was high, when a cold reserving material whose specific heat of 10K is low was used, it became clear by filling up only the low temperature side of regenerator with the above-mentioned cold reserving material in consideration of the temperature distribution inside regenerator that the refrigerator engine performance improved sharply by harnessing the high specific heat property in 4K of the cold reserving material.

[0018]

Moreover, in order to realize the above specific heat properties, this invention persons prepared the magnetic cold reserving material which has various presentations, and did comparative evaluation of the specific heat property. The result, especially this invention persons noted that the metallic compounds of germanium (germanium) and predetermined rare earth elements (R) had the peak of volume ratio heat in a low-temperature field as the magnetic substance.

Moreover, by permuting some germanium (germanium) by other elements, such as transition metals, the temperature of a specific heat peak and the width of face of a specific heat peak, and a configuration could be controlled, and it became clear that the high specific heat property in the degree region of low temperature made into the purpose was realizable for the first time.

This invention is completed based on the above-mentioned knowledge.

[0019]

That is, the cold reserving material concerning this invention is general formula:  $R_{1-x}(Ge_{1-y}M_y)_x$ . -- (1)

(However, R shows at least a kind of rare earth elements chosen from Y, La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb.) M shows at least a kind of element chosen from Ag, Au,

aluminum, Ga, In, Sn, Bi, Pd, Pt, Zn, Rh, Ir, Ru, Mn, Cr, Mo, W, V, Nb, Ta, Ti, Zr, and Hf.  $x$  and  $y$  are satisfied with an atomic ratio of  $0.1 \leq x \leq 0.8$  and  $0 \leq y \leq 0.5$ , respectively. It is characterized by consisting of the magnetic substance expressed.

[0020]

In the cold reserving material concerning above-mentioned this invention, it is desirable that the range of the atomic ratio  $x$  in said general formula is 0.5–0.7. Moreover, it is still more desirable that the range of the above-mentioned atomic ratio  $x$  is 0.6–0.7.

[0021]

Furthermore, in the above-mentioned cold reserving material, it is desirable that the particle size of the magnetic particle which constitutes a cold reserving material is 0.01–3mm.

Furthermore, in the above-mentioned cold reserving material, it is desirable that the rate of the magnetic particle which the ratio (aspect ratio) to the minor axis of a major axis is five or less, and has the particle size of 0.01mm or more 3mm or less to all the magnetic particles that constitute a cold reserving material is more than 70 mass %.

[0022]

Moreover, the cool storage type refrigerator concerning this invention has two or more cooling stages which consist of the regenerator filled up with the cold reserving material. In the cool storage type refrigerator which pours an actuation medium from the upper elevated-temperature side of the regenerator of each cooling stage, and obtains whenever [ low-temperature ] more in the downstream of regenerator by the heat exchange of the above-mentioned actuation medium and a cold reserving material. Some [ at least ] cold reserving materials of the cold reserving material with which the low temperature side space of the regenerator of an aftercooling stage is filled up are characterized by consisting of the cold reserving material expressed with said general formula:  $R1-x(\text{germanium}1-yMy) x$ . In addition, as for the cold reserving material of this invention, it is desirable that the down-stream low temperature side of regenerator is filled up.

[0023]

Furthermore, each of the MRI (Magnetic Resonance Imaging) equipment concerning this invention, super-conductive magnets for maglev trains, cryopumps, and field impression type crystal pulling equipments is characterized by providing the cool storage type refrigerator concerning above-mentioned this invention.

[0024]

The cold reserving material concerning this invention consists of the magnetic substance which consists of rare earth elements (R component) and germanium (germanium), or the magnetic substance which permuted some germanium (germanium) of the magnetic substance which has this basic presentation by other transition-metals elements etc. (M component) so that clearly from that general formula.

[0025]

The above-mentioned R components are at least one sort of rare earth elements chosen from Y, La, Ce, Pm, Sm, Eu, Gd, Tb, Dy, Tm, Er, and Yb. M component They are at least one sort of elements chosen from Ag, Au, aluminum, Ga, In, Sn, Bi, Pd, Pt, Zn, Rh, Ir, Ru, Mn, Cr, Mo, W, V, Nb, Ta, Ti, Zr, and Hf. When a part of germanium component is permuted, each of these R components and M components is added in order to move more the temperature location of the volume ratio thermal peak of the magnetic substance to a low temperature side, or to extend the full width at half maximum, or to adjust the specific heat property according to the design specification of a refrigerator and to realize the effective specific heat property as a cold reserving material.

[0026]

By choosing suitably the rare earth elements as the above-mentioned R component, the temperature location of the specific heat peak of the magnetic substance can be set to the target temperature, i.e., 4 – 6 K region.

[0027]

Let the amount  $x$  of permutations to R component of germanium containing the above-



mentioned M component be or more 0.1 0.8 or less range by the atomic ratio. When the above-mentioned amount x of permutations is less than 0.1, magnetic transition cannot be made to start in the target temperature field. On the other hand, if the above-mentioned amount x of permutations exceeds 0.8, the consistency of rare earth elements will fall remarkably and the magnetic specific heat will decrease. As for the atomic ratio x which shows the above-mentioned amount of permutations, it is desirable that it is the range of 0.5-0.7, and it is still more desirable that the range of the above-mentioned atomic ratio x is 0.6-0.7.

[0028]

Moreover, by permuting some germanium, the above-mentioned M component moves the temperature location of the specific heat peak of the magnetic substance, or extends the full width at half maximum, and it is added in order to adjust the specific heat property according to the design of a refrigerator. Let the amount y of permutations to germanium of the above-mentioned M component be or more 0 0.5 or less range by the atomic ratio. If the above-mentioned amount y of permutations exceeds 0.5, the volume ratio heat in the temperature region of 4 - 6K near [ target ] falls, and the temperature location of a specific heat peak will move greatly, the specific heat full width at half maximum will spread too much, height will fall, and functioning as a cold reserving material will become inadequate.

[0029]

As mentioned above, although R component shows a kind of predetermined rare earth elements at least, Gd, Tb, Dy, Ho, and its Er are desirable, and especially its Ho and Er are desirable.

[0030]

Moreover, although a kind of element chosen from Ag, Au, aluminum, Ga, In, Sn, Bi, Pd, Pt, Zn, Rh, Ir, Ru, Mn, Cr, Mo, W, V, Nb, Ta, Ti, Zr, and Hf is used at least as an M component, Ag, aluminum, Ga, In, and Sn are desirable.

[0031]

Moreover, while making smooth flow of actuation media, such as gaseous helium which flows the inside of the regenerator filled up with the cold reserving material, in order to raise the heat exchange effectiveness of the above-mentioned actuation medium and a cold reserving material and to maintain a heat exchange function to stability, the above-mentioned cold reserving material is good to constitute from a spherical magnetic particle to which particle size was equal. It is desirable to specifically adjust so that the rate of the magnetic particle which the ratio (aspect ratio) to the minor axis of a major axis is five or less, and has the particle size of 0.01mm or more 3mm or less to all the magnetic particles that constitute the above-mentioned cold reserving material may become more than 70% weight.

[0032]

It is the factor which does the big effect to the cooling function and heat-conducting characteristic of the reinforcement of a particle, and a refrigerator, and the pack density at the time of filling up regenerator, if the particle size is set to less than 0.01mm becomes high too much, and it will be accompanied to helium gas which passage resistance (pressure loss) of helium gas which is a cooling medium increases upwards rapidly, and circulates, and the particle size of a magnetic particle will invade in a compressor, and will wear a component part etc. at an early stage.

[0033]

On the other hand, when particle size exceeds 3mm, while producing a segregation in the crystalline structure of grain and becoming weak in it, the heating area between a magnetic particle and helium gas which is a cooling medium becomes small, and there is a possibility that heat transfer effectiveness may fall remarkably. Moreover, when such a big and rough particle exceeds 30 % of the weight, there is a possibility of causing cool storage performance degradation. Therefore, although mean particle diameter is set as 0.01mm or more 3mm or less, it is the range of 0.05-1.0mm more preferably, and 0.1 moremm or more 0.5mm or less is desirable. Moreover, in order to fully demonstrate a cooling function and reinforcement practically, it is desirable to the magnetic whole cold reserving material particle that the particle whose above-mentioned mean particle diameter is 0.01mm or more 3mm or less occupies 90%

or more still more preferably 80% of the weight or more preferably at least 70% of the weight or more.

[0034]

Moreover, the ratio (aspect ratio) of a major axis to the minor axis of a magnetic cold reserving material particle is preferably adjusted to 1.3 or less still much more preferably two or less still more preferably three or less five or less. The aspect ratio of a magnetic particle has a possibility of causing decline in cool storage effectiveness, when it has big effect on the pack density at the time of filling up the reinforcement and regenerator of a particle, and homogeneity, and an aspect ratio exceeds 5, it is high-density, it becomes difficult homogeneity and to be filled up at regenerator, as an opening becomes homogeneous and such a particle exceeds 30% of the weight of all cold reserving material particles, while a magnetic particle lifting-comes to be easy of deformation destruction with a mechanical work.

[0035]

In order that dispersion in the ratio of a major axis to dispersion and the minor axis of particle size of a magnetic particle which were prepared with the molten metal quenching method here may decrease greatly as compared with the case where it prepares by the conventional plasma-spraying method, there are few rates of the magnetic particle besides the above-mentioned size range. Moreover, when dispersion arises, it is also easy to use them, classifying them suitably. In this case, the rate of the magnetic particle of above-mentioned [ an aspect ratio ] within the limits can be preferably made into the cold reserving material which is fully equal to practical use by considering as 90% or more still more preferably 80% or more 70% or more among all the magnetic particles with which the cool storage section is filled up.

[0036]

Moreover, the long magnetic particle of a life can be extremely formed with high intensity setting the diameter of average crystal grain of the magnetic particle prepared with the molten metal quenching method as 0.5mm or less, or by making some [ at least ] metal textures amorphous.

[0037]

Moreover, the surface roughness of a magnetic particle is a factor which has big effect on a mechanical strength, a cooling property, passage resistance of a cooling medium, cool storage effectiveness, etc., and it is preferably desirable at maximum height  $R_{max}$  of the irregularity generally specified by JIS B0601 to set it as 2 micrometers or less still more preferably 5 micrometers or less 10 micrometers or less. In addition, such surface roughness can be measured with a scanning electron microscope (SEM granularity meter).

[0038]

If surface roughness exceeds 10microm $R_{max}$ , while becoming easy to generate the micro crack used as the starting point of destruction to a particle, passage resistance of a cooling medium will go up, the load of a compressor will increase, or the touch area of the magnetic particles with which it filled up especially will increase, migration of the cold energy between magnetic particles will become large, and cool storage effectiveness will fall.

[0039]

Moreover, the whole thing for which the rate of the magnetic particle which has the minute defect with a die length of 10 micrometers or more in which the mechanical strength of a magnetic particle is affected is preferably made 10% or less still more preferably 10% or less 30% or less is desirable practically.

[0040]

Especially the manufacture approach of a magnetic cold reserving material particle which was mentioned above is not limited, and can apply the various general-purpose alloy particle manufacture approaches. For example, while distributing the molten metal which has a predetermined presentation based on centrifugal atomization, the gas atomizing method, a rotational electrode process, etc., the approach (molten metal quenching method) of carrying out rapid solidification is applicable. Moreover, the approach of trickling a molten metal from the vibrating nozzle is also applicable.

[0041]

The cool storage type refrigerator concerning this invention fills up with the above-mentioned magnetic cold reserving material particle a part of regenerator [ at least ] of the aftercooling stage of a refrigerator which has two or more cooling stages, and is constituted. For example, in a two-step expansion type refrigerator, in a three-step expansion type refrigerator, while being filled up with the magnetic cold reserving material particle which starts this invention at low-temperature one end of the 3rd step regenerator, other cold reserving material restoration space is filled up with other cold reserving materials which have a specific heat property according to the temperature distribution, and it is constituted by low-temperature one end of the 2nd step regenerator in it again.

[0042]

When too little [ at the rate of a volume ratio / the fill of the magnetic cold reserving material particle of this invention in the low temperature side space of the regenerator of the aftercooling stage mentioned above / as less than 3% ], improvement in the cool storage effectiveness of a refrigerator is not accepted, and the capacity of a refrigerator is not improved. On the other hand, if it becomes excessive so that a fill may exceed 70 volume %, the fault of the specific heat property of the magnetic cold reserving material particle mentioned above will become remarkable, and will cause decline in cool storage effectiveness similarly. that is, as a result of it having a bad influence on the whole regenerator that the volume ratio heat in temperature regions other than the temperature from which volume ratio heat serves as a peak, especially an elevated-temperature side temperature region is comparatively alike, and becomes small, decline in cool storage effectiveness is caused. Therefore, although the rate of a restoration volume ratio of the magnetic cold reserving material particle of this invention to the complete product of the regenerator of the above-mentioned aftercooling stage is made into the range of 3 - 70 volume %, it is the range of 5 - 50 volume % preferably, and especially its range of further 10 - 30 volume % is desirable.

[0043]

The rare earth-germanium system magnetic material which has the peak of steep volume ratio heat in a super-low temperature range according to the cold reserving material concerning the above-mentioned configuration, Or since a part of the constituent germanium is constituted from an  $R1-x(\text{germanium}1-y\text{My})x$  system magnetic material permuted by other transition-metals elements etc., while the temperature location of a volume ratio thermal peak shifts to a low temperature side more, the specific heat full width at half maximum is expanded, and a cold reserving material with a good specific heat property is obtained. And by filling up the cold reserving material with the predetermined rate of a volume ratio into low-temperature one end in the regenerator which constitutes the aftercooling stage of a refrigerator, the refrigerating capacity in temperature 4 K region is high, and can offer the refrigerator which can maintain the frozen engine performance continued and stabilized at the long period of time.

[0044]

And each of the MRI equipment of this invention using a refrigerator with which the refrigerator engine performance mentioned above each of MRI equipment, cryopumps, super-conductive magnets for maglev trains, and field impression type crystal pulling equipments from influencing the engine performance of each equipment, cryopumps, super-conductive magnets for maglev trains, and field impression type crystal pulling equipments can demonstrate the engine performance which continued and was excellent in the long period of time.

[0045]

[Embodiment of the Invention]

Next, the operation gestalt of this invention is concretely explained based on the example shown below.

[0046]

(Example 1)

Er<sub>0.375</sub>germanium<sub>0.625</sub> hardener was produced by the RF dissolution. This

Er<sub>0.375</sub>germanium<sub>0.625</sub> hardener is fused by about 1400 K, and among helium ambient

atmosphere (pressure: 90kPa), this molten metal was dropped on the disk which rotates by 1x104rpm, and carried out rapid solidification. After the aspect ratio carried out configuration classification of the 1.2 or less particle from the obtained magnetic-substance particle, by carrying out screen analysis, it considered as the cold reserving material which prepares 200g of spherical particles with a particle size of 0.2-0.3mm, and starts an example 1.

[0047]

In order to evaluate the property of the cold reserving material prepared as mentioned above on the other hand, the two-step expansion type GM refrigerator as shown in drawing 1 was prepared. In addition, the GM refrigerator 10 of a two-step type shown in drawing 1 shows one example of the refrigerator of this invention. the GM refrigerator 10 of a two-step type shown in drawing 1 -- a major diameter -- it has the 1st cylinder of 11 and the vacuum housing 13 of this minor diameter connected with 11 in same axle the 1st cylinder in which 12 [ cylinder / 2nd ] was installed. The 1st regenerator 14 is arranged by 11 free [ reciprocation ], and the 2nd cylinder of the 1st cylinder of the 2nd regenerator 15 is arranged free [ reciprocation ] 12. Between the 1st cylinder 11 and the 1st regenerator 14, it reaches and the 2nd cylinder of seal rings 16 and 17 is arranged between 12 and the 2nd regenerator 15, respectively.

[0048]

The 1st cold reserving material 18, such as Cu mesh, is held in the 1st regenerator 14. The cold reserving material for very low temperature of this invention is filled up into the bass side of the 2nd regenerator 15 with the predetermined ratio as the 2nd cold reserving material 19. The 1st regenerator 14 and the 2nd regenerator 15 have the path of actuation media, such as helium gas formed in the gap of the 1st cold reserving material 18 or the cold reserving material 19 for very low temperature etc., respectively.

[0049]

The 1st expansion chamber 20 is formed between the 1st regenerator 14 and the 2nd regenerator 15. Moreover, the 2nd cylinder of the 2nd expansion chamber 21 is formed between the tip walls of 12 with the 2nd regenerator 15. And the low-temperature 2nd cooling stage 23 is formed in the pars basilaris ossis occipitalis of the 1st expansion chamber 20 for the 1st cooling stage 22 from the 1st cooling stage 22 again at the pars basilaris ossis occipitalis of the 2nd expansion chamber 21.

[0050]

A high-pressure actuation medium (for example, helium gas) is supplied to the GM refrigerator 10 of a two-step type which was mentioned above from a compressor 24. The supplied actuation medium passes through between the 1st cold reserving material 18 held in the 1st regenerator 14, reaches the 1st expansion chamber 20, passes through between the cold reserving materials 19 for very low temperature (the 2nd cold reserving material) further held in the 2nd regenerator 15, and reaches the 2nd expansion chamber 21. In this case, an actuation medium supplies heat energy to each cold reserving materials 18 and 19, and is cooled. Each cold reserving material 18 and the actuation medium which passed through between 19 expand by each expansion chambers 20 and 21, chill is generated, and each cooling stages 22 and 23 are cooled. The actuation medium which expanded flows between each cold reserving material 18 and 19 to an opposite direction. After an actuation medium receives heat energy from each cold reserving materials 18 and 19, it is discharged. The thermal efficiency of an actuation medium cycle improves, and it is constituted so that still lower temperature may be realized, as the recuperation effectiveness becomes good in such a process.

[0051]

And the low temperature side of the 2nd step regenerator of the above-mentioned two-step expansion type GM refrigerator was filled up with 200g of cold reserving materials concerning the example 1 prepared as mentioned above. Furthermore, to the elevated-temperature side, the refrigerator which is filled up with 100g and starts an example 1 in Pb was assembled.

[0052]

And as a result of carrying out a freezing test about the refrigerator concerning the example 1 assembled as mentioned above and measuring the refrigerating capacity after 3000-hour

continuous running, 1.11W were obtained as refrigerating capacity in 4.2K.

[0053]

In addition, the refrigerating capacity in this example made the thermal load act on the 2nd cooling stage at a heater at the time of refrigerator operation, and the thermal load when the temperature rise of the 2nd cooling stage stops by 4.2K defined it.

[0054]

(Example 2)

Er<sub>0.375</sub>germanium<sub>0.325</sub>Sn<sub>0.3</sub> hardener was produced by the RF dissolution. This Er<sub>0.375</sub>germanium<sub>0.325</sub>Sn<sub>0.3</sub> hardener is fused by about 1450 K, and among helium ambient atmosphere (pressure: 90kPa), this molten metal was dropped on the disk which rotates by 1x10<sup>4</sup>rpm, and carried out rapid solidification. After the aspect ratio carried out configuration classification of the 1.2 or less particle from the obtained magnetic-substance particle, by carrying out screen analysis, the cold reserving material which prepares 200g of spherical particles with a particle size of 0.2-0.3mm, and starts an example 2 was obtained. The low temperature side of the 2nd step regenerator of a two-step expansion type GM refrigerator was filled up with this. In the elevated-temperature side, the cool storage type refrigerator which is filled up with 100g of Pb(s) and starts an example 2 was assembled.

[0055]

And as a result of carrying out a freezing test like an example 1, 1.05W were obtained as refrigerating capacity in 4.2K.

[0056]

(Example 3)

Er<sub>0.2</sub>Ho<sub>0.175</sub>germanium<sub>0.625</sub> hardener was produced by the RF dissolution. This Er<sub>0.2</sub>Ho<sub>0.175</sub>germanium<sub>0.625</sub> hardener is fused by about 1400 K, and among helium ambient atmosphere (pressure: 90kPa), this molten metal was dropped on the disk which rotates by 1x10<sup>4</sup>rpm, and carried out rapid solidification. After the aspect ratio carried out configuration classification of the 1.2 or less particle from the obtained magnetic-substance particle, by carrying out screen analysis, 200g of spherical particles with a particle size of 0.2-0.3mm was prepared, and it considered as the cold reserving material concerning an example 3. The low temperature side of the 2nd step regenerator of a two-step expansion type GM refrigerator was filled up with this. In the elevated-temperature side, the cool storage type refrigerator which is filled up with 100g of Pb(s) and starts an example 3 was assembled.

[0057]

And as a result of carrying out a freezing test like an example 1, 1.05W were obtained as refrigerating capacity in 4.2K.

[0058]

(Example 1 of a comparison)

The hardener which has a presentation conventionally which becomes HoCu<sub>2</sub> by the RF dissolution was produced. This HoCu<sub>2</sub> hardener is fused by about 1350 K, and among helium ambient atmosphere (pressure: 90kPa), this molten metal was dropped on the disk which rotates by 1x10<sup>4</sup>rpm, and carried out rapid solidification. After the aspect ratio carried out configuration classification of the 1.2 or less particle from the obtained magnetic-substance particle, by carrying out screen analysis, it considered as the cold reserving material which prepares 200g of spherical particles with a particle size of 0.2-0.3mm, and starts the example 1 of a comparison. The low temperature side of the 2nd step regenerator of a two-step expansion type GM refrigerator was filled up with this. In the elevated-temperature side, the cool storage type refrigerator which is filled up with 100g and starts the example 1 of a comparison in Pb was assembled.

[0059]

And as a result of carrying out a freezing test like an example 1, 0.69W were obtained as refrigerating capacity in 4.2K.

[0060]

In the refrigerator which used the cold reserving material of each example which consists of the

magnetic substance which permuted some of Er-germanium magnetic substance (example 1) or germanium by the transition-metals element etc., all have checked that the refrigerating capacity in 4 K region became high also 1.5 to 1.7 times as compared with the thing of the example 1 of a comparison so that clearly from the measurement result of the refrigerating capacity in each refrigerator. In the refrigerator which used the cold reserving material which furthermore starts each example, since the mechanical strength of a cold reserving material increased, there was little degradation, there were few falls of refrigerating capacity after prolonged continuous running, and it became clear that the stable refrigerating capacity was maintainable.

[0061]

Next, the example of the superconduction MRI equipment which used the cool storage type refrigerator concerning this invention, the super-conductive magnet for maglev trains, cryopump, and field impression type crystal pulling equipment is described.

[0062]

Drawing 2 is the sectional view showing the outline configuration of the superconduction MRI equipment which applied this invention. The superconduction MRI equipment 30 shown in drawing 2 is constituted by the superconduction static magnetic field coil 31 which is uniform and impresses a stable static magnetic field in time spatially to the body, the amendment coil which omitted the illustration which amends the heterogeneity of a generating field, the inclination field coil 32 which gives field inclination to a measurement field, and the probe 33 grade for radio wave transmission and reception. And the cool storage type refrigerator 34 which starts this invention which was mentioned above as an object for cooling of the superconduction static magnetic field coil 31 is used. In addition, 35 in drawing is a cryostat and 36 is radiation heat insulation shielding.

[0063] In the superconduction MRI equipment 30 using the cool storage type refrigerator 34 concerning this invention, since it can continue at a long period of time and the operating temperature of the superconduction static magnetic field coil 31 can be guaranteed to stability, spatially, uniformly and in time, it can continue and a stable static magnetic field can be obtained at a long period of time. Therefore, it becomes possible to continue, to be stabilized and to demonstrate the engine performance of superconduction MRI equipment 30 at a long period of time.

[0064]

Drawing 3 is the perspective view showing the important section outline configuration of the super-conductive magnet for maglev trains which used the cool storage type refrigerator concerning this invention, and shows the part of the superconduction magnet 40 for maglev trains. The superconduction magnet 40 for maglev trains shown in drawing 3 is constituted by the cool storage type refrigerator 44 grade concerning the liquid helium tank 42 for cooling the superconduction coil 41 and this superconduction coil 41, the liquid nitrogen tank 43 which prevents the vaporization of this liquid helium tank, and this invention. In addition, as for a laminating heat insulator and 46, 45 in drawing is [ a power lead and 47 ] permanent current switches.

[0065]

In the superconduction magnet 40 for maglev trains using the cool storage type refrigerator 44 concerning this invention, since it can continue at a long period of time and the operating temperature of the superconduction coil 41 can be guaranteed to stability, it continues, and it is stabilized and the magnetic levitation of a train and a field required for promotion can be acquired at a long period of time. Since especially the cool storage type refrigerator 44 that starts this invention although acceleration acts with the superconduction magnet 40 for maglev trains can maintain the refrigerating capacity which continued and was excellent in the long period of time when acceleration acts, it contributes to long-term stabilization of magnetic field strength etc. greatly. Therefore, it becomes possible to continue and to demonstrate the dependability of the maglev train using such a superconduction magnet 40 at a long period of time.

[0066]

Drawing 4 is the sectional view showing the outline configuration of the cryopump which used the cool storage type refrigerator concerning this invention. The cryopump 50 shown in drawing 4 is constituted by the ring 55 grade to which exhaust velocity, such as the cryopanel 51 which condenses or adsorbs a gas molecule, the cool storage type refrigerator 52 concerning this invention which cools this cryopanel 51 to predetermined very low temperature, the shielding 53 prepared among these, the baffle 54 formed in the inlet and an argon, nitrogen, and hydrogen, is changed.

[0067]

In the cryopump 50 using the cool storage type refrigerator 52 concerning this invention, it can continue at a long period of time, and the operating temperature of a cryopanel 51 can be guaranteed to stability. Therefore, it becomes possible to continue, to be stabilized and to demonstrate the engine performance of cryopump 50 at a long period of time.

[0068]

Drawing 5 is the perspective view showing the outline configuration of the field impression type crystal pulling equipment which used the cool storage type refrigerator concerning this invention. The field impression type crystal pulling equipment 60 shown in drawing 5 is constituted by the elevator style 63 grade of the crystal pulling section 61 which has the crucible for raw material melting, a heater, a crystal pulling device, etc., the superconduction coil 62 which impresses a static magnetic field to raw material melt, and the crystal pulling section 61. And the cool storage type refrigerator 64 which starts this invention which was mentioned above as an object for cooling of the superconduction coil 62 is used. In addition, as for a current lead and 66, 65 in drawing is [ a heat-shield plate and 67 ] helium containers.

[0069]

In the field impression type crystal pulling equipment 60 using the cool storage type refrigerator 64 concerning this invention, since it can continue at a long period of time and the operating temperature of the superconduction coil 62 can be guaranteed to stability, it can continue and the good field which suppresses the convection current of the raw material melt of a single crystal can be acquired at a long period of time. Therefore, it becomes possible to continue, to be stabilized and to demonstrate the engine performance of field impression type crystal pulling equipment 60 at a long period of time.

[0070]

[Effect of the Invention]

The R-germanium magnetic material which has the peak of steep volume ratio heat in a super-low temperature range according to the cold reserving material which starts this invention above as explanation, Or since a part of the main constituent is constituted from an  $R1-x(\text{germanium}1-y\text{My})x$  system magnetic material permuted by other rare earth elements or transition-metals elements etc., while the temperature location of a volume ratio thermal peak shifts to a low temperature side more The specific heat full width at half maximum is expanded, and a cold reserving material with a good specific heat property is obtained. And by filling up with the cold reserving material low-temperature one end in the regenerator which constitutes the aftercooling stage of a refrigerator, the refrigerating capacity in temperature 4 K region is high, and can offer the refrigerator which can maintain the frozen engine performance continued and stabilized at the long period of time.

[0071]

Therefore, the refrigerator of this invention using such a cold reserving material for very low temperature becomes possible [ continuing and maintaining the outstanding frozen engine performance with sufficient repeatability at a long period of time ]. Moreover, the MRI equipment of this invention which has such a refrigerator, cryopump, the super-conductive magnet for maglev trains, and field impression type crystal pulling equipment can demonstrate the engine performance which continued and was excellent in the long period of time.

[Brief Description of the Drawings]

[Drawing 1] The sectional view showing the important section configuration of the cool storage

type refrigerator (GM refrigerator) concerning this invention.

[Drawing 2] The sectional view showing the outline configuration of the superconduction MRI equipment by one example of this invention.

[Drawing 3] The perspective view showing the important section outline configuration of the super-conductive magnet (for maglev trains) by one example of this invention.

[Drawing 4] The sectional view showing the outline configuration of the cryopump by one example of this invention.

[Drawing 5] The perspective view showing the important section outline configuration of the field impression type crystal pulling equipment by one example of this invention.

[Description of Notations]

10 GM Refrigerator (Cool Storage Type Refrigerator)

11 1st Cylinder

12 2nd Cylinder

13 Vacuum Housing

14 1st Regenerator

15 2nd Regenerator

16 17 Seal ring

18 1st Accumulation Material

19 2nd Accumulation Material (Cold Reserving Material for Very Low Temperature)

20 1st Expansion Chamber

21 2nd Expansion Chamber

22 1st Cooling Stage

23 2nd Cooling Stage

24 Compressor

30 Superconduction MRI Equipment

31 Superconduction Static Magnetic Field Coil

32 Inclination Field Coil

33 Probe for Radio Wave Transmission and Reception

34 Cool Storage Type Refrigerator

35 Cryostat

36 Radiation Heat Insulation Shielding

40 Super-conductive Magnet (Magnet)

41 Superconduction Coil

42 Liquid Helium Tank

43 Liquid Nitrogen Tank

44 Cool Storage Type Refrigerator

45 Laminating Heat Insulator

46 Power Lead

47 Permanent Current Switch

50 Cryopump

51 Cryopanel

52 Cool Storage Type Refrigerator

53 Shielding

54 Baffle

55 Ring

60 Field Impression Type Crystal Pulling Equipment

61 Crystal Pulling Section

62 Superconduction Coil

63 Elevator Style

64 Cool Storage Type Refrigerator

65 Current Lead

66 Heat-shield Plate

67 Helium Container



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[Translation done.]

## \* NOTICES \*

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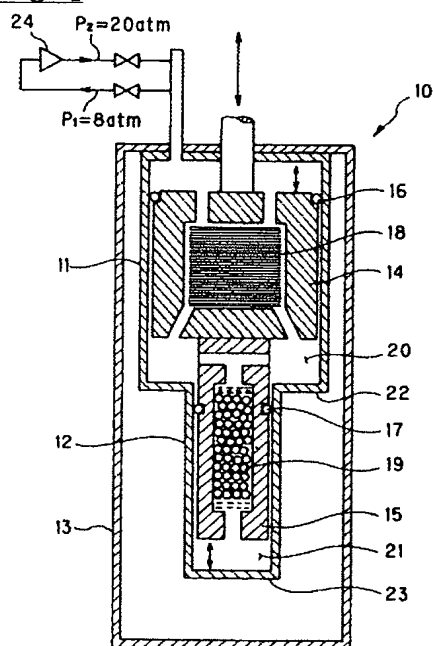
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2.\*\*\* shows the word which can not be translated.

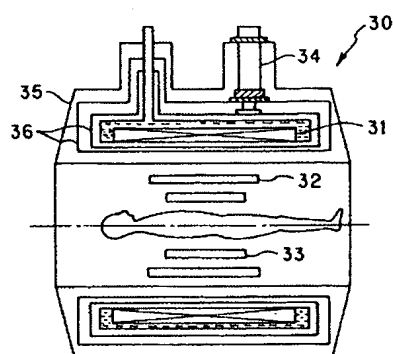
3.In the drawings, any words are not translated.

## DRAWINGS

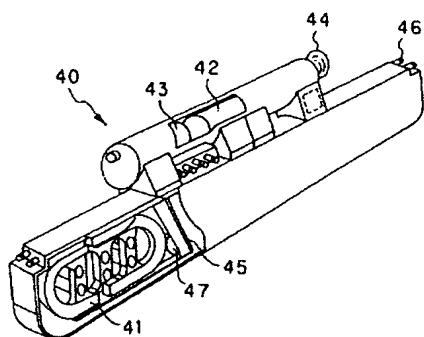
[Drawing 1]



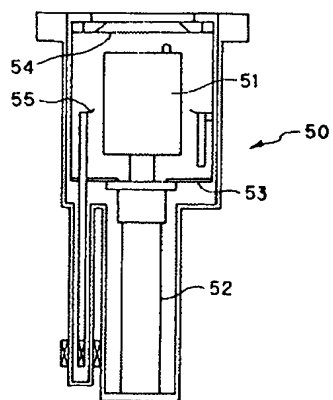
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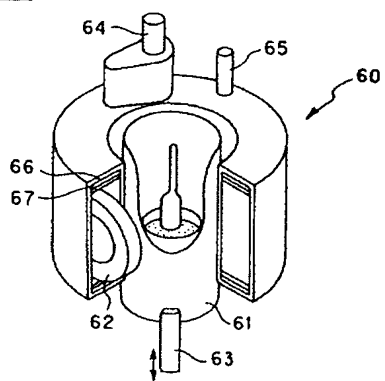
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]